Science of the Total Environment 644 (2018) 68–76

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Characterisation of dissolved organic matter using Fourier-transform ion cyclotron resonance mass spectrometry: Type-specific unique signatures and implications for reactivity

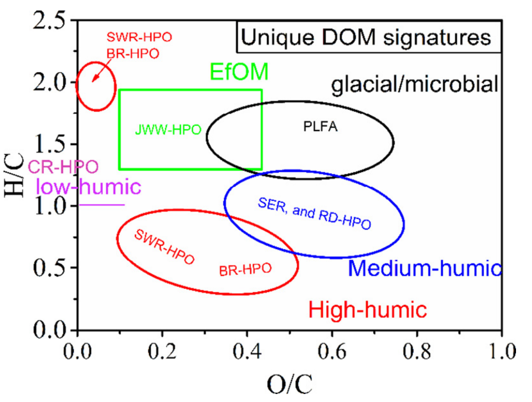
Xi-Zhi Niu [a,*], Mourad Harir [b,c], Philippe Schmitt-Kopplin [b,c], Jean-Philippe Croué [a,*]

[a] *Curtin Water Quality Research Centre, Department of Chemistry, Curtin University, GPO Box U1987, Perth, WA 6845, Australia*
[b] *Analytical BioGeoChemistry, German Research Centre for Environmental Health, Helmholtz Zentrum München, Ingolstädter landstrasse. 1, 85764 Neuherberg, Germany*
[c] *Chair of Analytical Food Chemistry, Technische Universität München, Freising-Weihenstephan, Germany*

HIGHLIGHTS

- 957 common formulas observed for eight surface water DOMs
- Unique chemical signatures of different DOM types synthesized
- Double bond equivalent correlated to $SUVA_{254}$
- Comparing elemental analysis and FTICR-MS results of DOM
- Type-specific unique signatures have important implications for DOM reactivity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 May 2018
Received in revised form 28 June 2018
Accepted 28 June 2018
Available online xxxx

Editor: D. Barcelo

Keywords:
Fourier-transform ion cyclotron resonance mass spectrometry
Dissolved organic matter characterisation
Unique signatures
Elemental analysis
Specific ultraviolet-visible absorbance

ABSTRACT

This study investigated the chemodiversity and unique signatures for dissolved organic matter (DOM) from different types of water using high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). Eight freshwater hydrophobic DOM (HPO) share 10–17% formulas that were mainly lignin-like compounds. Unique signatures were synthesized: unique to the high-humic HPO (Suwannee River and Blavet River) were condensed aromatic and some aliphatic compounds with $H/C > 1.5$ and $O/C < 0.2$, which is considered as decisive of these black river water. Medium-humic isolates (Loire River, Seine River, South Platte River, and Ribou Dam) did not show explicit unique signatures. Nonetheless, enhanced chemodiversity was observed for medium-humic isolates extracted from a variety of indigenous environmental conditions. As an example, South Platte River HPO isolated in winter showed signatures similar to low-humic HPO (Colorado River), i.e., predominantly aliphatic CHO ($H/C > 1.0$). Effluent HPO was mainly aliphatic molecules with $0.2 < O/C < 0.5$ and enriched in S-bearing molecules, and molecules unique to glacial DOM (Pony Lake) incorporated N-bearing compounds that were inferiorly oxidized and were considered as microbial-derived. The weight-averaged double bond equivalent and elemental ratio derived from FTICR-MS were compared with $SUVA_{254}$ and the results from elemental analysis. This acts as the first study to synthesize unique chemical compositions

---

* Corresponding authors.
E-mail addresses: xi-zhi.niu@postgrad.curtin.edu.au, (X.-Z. Niu), jean-philippe.croue@curtin.edu.au (J.-P. Croué).

https://doi.org/10.1016/j.scitotenv.2018.06.351

that distinguish different types of DOM and determine certain reactivity. It is also a significant reference for future studies using similar types of DOM.

1. Introduction

The heterogeneous composition of dissolved organic matter (DOM) is influenced by the source of the organic compounds, i.e., allochthonous and autochthonous (Croué, 2004; Leenheer and Croué, 2003), and is impacted by indigenous abiotic and biotic processes (Gonsior et al., 2009; Seidel et al., 2014; Sleighter et al., 2014). Knowledge on the composition of DOM has been considered a research priority since DOM plays numerous roles in the environment, including but not limited to mediating the fate of anthropogenic chemicals (Borch et al., 2009; Cooper et al., 1989; Ravichandran, 2004), altering photochemical and photophysical processes (Lundeen et al., 2016; McNeill and Canonica, 2016; Niu et al., 2016), and interactions with biota (Ducklow and Carlson, 1992). DOM also impacts the quality of potable water, especially as a precursor of disinfection by-products (Singer, 1999). Notwithstanding its complex and dissimilar nature, continuous efforts have been devoted to characterise DOM and link DOM characteristics to its behaviour in the natural environment and along drinking water treatment processes.

At present, several approaches have been widely used to characterise DOM. For examples, when analysed in water (i.e., direct analysis), specific UV absorbance ($SUVA_{254}$) acquired with TOC and UV–visible absorbance at 254 nm strongly correlates to the degree of unsaturation and aromatic content (Weishaar et al., 2003). Fluorescent measurement and the application of parallel factor analysis (PARAFAC) helped reveal the major components of DOM (Andersen and Bro, 2003; Chen et al., 2003; Coble, 1996). Chromatography facilities such as SEC (size exclusion chromatography)-UV, DOC, and DON (Dissolved Organic Nitrogen) detections (LC-UV-OCD-OND) have been commonly used to characterise DOM of a variety of source waters (Bruchet et al., 1990; Chin et al., 1994; Huber et al., 2011; Lee et al., 2004). When isolated/purified and available as powder, DOM can be characterised by pyrolysis/thermochemolysis GC/MS, solid state NMR (nuclear magnetic resonance spectroscopy), elemental analysis, and FTIR (Fourier-transform infrared spectroscopy) (Croué, 2004; Leenheer and Croué, 2003). Following electrospray ionization, FTICR-MS (Fourier transform ion cyclotron resonance mass spectrometry) gained increasing interest from the scientific community due to its ultra-high mass resolution. To date, FTICR-MS has contributed to the characterisation of DOM from various origins, including the well-known Suwannee River fulvic acid (D'Andrilli et al., 2013; Hertkorn et al., 2008), Antarctic DOM (Cawley et al., 2016; D'Andrilli et al., 2013), dissolved algal organic materials (Zhang et al., 2014), effluent organic matter (Gonsior et al., 2011), marine DOM (Koch et al., 2008), and many other aquatic DOM of miscellaneous inputs (Gonsior et al., 2017; Gonsior et al., 2016; Kamjunke et al., 2017; Luek et al., 2017; Sleighter et al., 2014).

Innumerable DOM from various global sources have been characterised, and obviously the number of these studies is still rapidly increasing. According to these studies, DOM from similar types of water seemed to possess comparable reactivity. Although the DOM sources of each watershed are unlikely identical, distinct water type (e.g., black river water, low-humic water, wastewater effluent) could have unique chemical signatures that decide their uniqueness in reactivity. To our knowledge, there are few comprehensive characterisation study covering DOM from various water types and illustrating the chemodiversity and the type-specific unique signatures. In the current investigation, nine DOM isolates of five categories (i.e., high-humic, medium-humic, and low-humic from surface waters, wastewater effluent, and glacial water) were characterised using FTICR-MS. The chemical similarity, diversity, and unique signature for each DOM type were identified. Subsequently, the unique signatures were discussed in correlation to DOM reactivity in aquatic processes. This investigation also evaluated the correlations of the elemental ratio and double bond equivalent (DBE) deduced from FTICR-MS versus elemental analysis and $SUVA_{254}$.

2. Materials and methods

2.1. DOM isolates

This study was performed on nine DOM fractions, Pony Lake fulvic acid (PLFA) from the International Humic Substances Society and eight previously extracted and characterised (e.g., $SUVA_{254}$, solid state NMR, elemental analysis) DOM isolates from seven fresh waters and one urban treated wastewater (Croué, 2004; Croue et al., 2000; Hwang et al., 2001; Niu et al., 2014; Zheng et al., 2014). Hydrophobic DOM (HPO) fractions were isolated using the XAD-8® resin (Rohm and Hass) (Leenheer et al., 2000a). PLFA can be considered as HPO DOM. The acronyms, site information, percent DOC recovery, and $SUVA_{254}$ of these isolates are provided in Table 1.

2.2. High-resolution mass spectrometry FTICR-MS

Negative electrospray ionization Fourier transform ion cyclotron resonance [ESI(−)] FTICR mass spectra were acquired using a 12T Bruker Solarix mass spectrometer (Bruker Daltonics, Bremen, Germany) and an Apollo II electrospray ionization (ESI) source in negative mode (Cawley, 2016). The concentrations of the HPO fractions were prepared in methanol for direct infusion using a microliter pump at a flow rate of 120 μL h^{-1} with a nebulizer gas pressure of 138 kPa and a drying gas pressure of 103 kPa. A source heater temperature of 200 °C was maintained to ensure rapid desolvation of the ionized droplets. The spectra were acquired with a time domain of 4 MW in [ESI(−)], and 500 scans were accumulated for each mass spectrum. All spectra were internally calibrated using DOM reference mass list. Data processing was conducted using Compass Data Analysis 4.0 (Bruker, Bremen, Germany) and formula assignment was processed by in-house made software (NetCalc) (Tziotis et al., 2011). Molecular formula assignments were generated based on the exact mass differences using NetCalc software (Tziotis et al., 2011). The assigned molecular formulas were based on a restricted list of selected small molecular units with defined mass differences (Tziotis et al., 2011). Molecular formula assignments correspond to a multiple Kendrick analogue mass defect analysis and

Table 1
Origins, acronyms, and $SUVA_{254}$ of DOM isolates.

Isolate name	Sampling location	Recovery (%)[b]	[c]$SUVA_{254}$
BR-HPO[a]	Blavet River (Kerne Uhel-Finistere, France)	55	5.1
SWR-HPO	Suwannee River (Okeefenokee Swamp, GA, USA)	77	4.6
RD-HPO	Ribou Dam (Cholet, Maine et Loire, France)	59	3.4
LR-HPO	Loire River (Belleville-sur-Loire, Cher, France)	57	3.1
SER-HPO	Seine River (Vigneux, upstream Paris city, France)	44	2.5
SPR-HPO	South Platte River (Waterton Canyon, CO, USA)	31	2.9
CR-HPO	Colorado River (Southern California, USA)	42	1.8
PLFA	Pony Lake (Ross Island, Antarctica)	17.5–21	3.0
JWW-HPO	Jeddah Wastewater effluent, (Jeddah, Saudi Arabia)	39	3.3

[a] Hydrophobic fraction (isolated from XAD-8® resin, Rhom and Hass).

[b] The percent of total dissolved organic carbon in the HPO extracts.

[c] Unit: L mg C^{-1} m^{-1}.